High Temperature Behaviour of Strontium Uranates

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High temperature behaviour of strontium uranates has been studied by means of X-ray powder diffractometry, thermogravimetry, differential thermal analysis, dilatometry and high temperature X-ray diffractometry. Six compounds of strontium uranates, viz. Sr$_3$UO$_6$, Sr$_2$UO$_5$, Sr$_2$UO$_4$, SrUO$_4$, SrU$_2$O$_7$, and Sr$_2$U$_3$O$_9$ have been identified in the temperature range of 1273-1673 K in air. The thermogravimetric analysis of these compounds carried out in the temperature range up to 1623 K shows that the decomposition temperature of strontium uranates decreases with decrease in strontium content. The results of DTA in the temperature range up to 1573 K show that in case of Sr$_2$UO$_4$ there is a reversible transition which is attributed to Sr$_3$UO$_6$ (monoclinic) = Sr$_2$UO$_5$ (orthorhombic) and in the case of Sr$_2$U$_3$O$_9$ there is decomposition of the parent compound to Sr$_2$U$_3$O$_7$ and U$_3$O$_7$. The results of thermal expansion studies carried out in the temperature range up to 1273 K show that the average linear and volume thermal expansion coefficients of the compounds Sr$_2$UO$_4$, Sr$_2$UO$_5$, Sr$_2$U$_3$O$_7$, SrUO$_4$, and SrU$_2$O$_7$ are nearly the same ($\alpha = 10^{-13}$ $x 10^{8}$K$^{-1}$ and $\alpha = 29-33 \times 10^{-8}$K$^{-1}$). However, the thermal expansion coefficient of Sr$_2$U$_3$O$_9$ shows an increase ($\alpha = 17.4 \times 10^{-8}$K$^{-1}$ and $\alpha = 47.2 \times 10^{-8}$K$^{-1}$) and for the compound Sr$_2$U$_3$O$_7$ it shows a sudden decrease ($\alpha = 0.5 \times 10^{-8}$K$^{-1}$ and $\alpha = -13.7 \times 10^{-8}$K$^{-1}$).

The binary strontium oxide-uranium oxide system is quite complex in which no less than six compounds are formed. The strontium uranates known in the literature are Sr$_3$UO$_6$, Sr$_2$UO$_5$, Sr$_2$UO$_4$, SrUO$_4$, SrU$_2$O$_7$, and Sr$_2$U$_3$O$_9$.

While many investigators have reported the preparation and characterization of strontium uranates, very little is known about their thermal behaviour at high temperatures. Studies in the binary strontium oxide-uranium oxide system in air were, therefore, undertaken. For this purpose, different strontium uranates were prepared and characterized by chemical and physical methods and their high temperature behaviour was studied by means of X-ray powder diffractometry, thermogravimetry, differential thermal analysis, dilatometry and high temperature X-ray diffractometry. The results of these studies are reported here.

Materials and Methods

The strontium uranates were prepared using strontium nitrate (E. Merck, GR) and nuclear pure U$_3$O$_8$.

Appropriate quantities of the carefully ground mixtures of Sr(NO$_3$)$_2$ and UO$_2$ to give the desired mole % of Sr/O and U/O were heated at different temperatures in the range 1273-1673 K for a period of 24 hr in air. The samples were air-quenched after the desired period of heating and ground to -200 mesh. This process was repeated if required.

Philips wide angle diffractometer with filtered CuK$_\alpha$ radiation (34 kV, 18 mA) was used for the identification of phases. A scanning speed of 12$^\circ$ 28/min was used.

For the determination of cell parameters, a slower scanning speed of 1/4$^\circ$ 28/min was used. The accurate values of cell parameters were obtained using the computer programme for least square refinement method.

The composition of the compounds was determined by chemical analysis. Strontium was determined gravimetrically as SrSO$_4$ while total uranium, and oxygen to uranium ratio were determined volumetrically.

Stanton (model HT) automatic recording thermobalance of 1 mg sensitivity and range up to 1623 K was used for the thermogravimetric analysis. The TG curves were recorded with about 1 g of each sample at a constant heating rate of 10 K/minute.

Differential thermal analysis was carried out in the temperature range up to 1573 K, the maximum temperature attainable with the present DTA equipment. DTA curves were recorded using about 500 mg of the sample with a recorder span of 0.5 mV. A constant linear heating rate of 10 K/min was used. Calcined alumina was used as a reference material.

Thermal expansion measurements were carried out employing dilatometric and high temperature X-ray diffractometric techniques in the temperature range up to 1273 K. Type LKB 3185 dilatometer with a constant heating rate of 4 K/min was used for dilatometric studies. Samples in the form of pellets (10 x 12.5 mm) were used. The pellets were sintered in air for 24 hr at 1273 K. For high temperature X-ray diffractometric studies, MRC model X-86-N3 high temperature X-ray diffractometer attachment mounted on a Philips wide angle goniometer was used. The high temperature X-ray powder diffraction patterns were recorded at different temperatures in the range of 298-1273 K in air using CuK$_\alpha$ radiation (34 kV, 18 mA). Temperature control was maintained by the MRC X-8600-5000-2 proportional temperature controller.
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Results and Discussion

The various phases identified in the system SrO-UO₂ in the temperature range of 1273-1673 K and the composition range of 25 to 80 at % (uranium + strontium) are schematically shown in Fig. 1.

The same six compounds of strontium uranates, viz. Sr₃UO₆, Sr₂UO₇, SrUO₄, Sr₂U₄O₁₁ and Sr₂U₅O₁₈, as reported earlier1,2 were obtained in this temperature range in air. The schematic phase diagram (Fig. 1) is in good agreement with that given by Bisi et al.3.

The results of the cell parameter determinations as well as the chemical analysis of the strontium uranates are summarized in Table 1.

In TGA no weight loss is observed for the compounds Sr₃UO₆, Sr₃U₂O₇, and Sr₂U₂O₅ in the entire temperature range studied, i.e. 298-1623 K in air. However, for the compounds Sr₂U₂O₇, Sr₂U₅O₁₁, and Sr₂U₇O₃₈ the temperature for inception of weight loss due to decomposition decreased with decreasing strontia content and was about 1593 K, 1533 K and 1433 K respectively. The weight losses observed for the compounds Sr₃UO₆, Sr₂U₅O₁₁, and Sr₂U₇O₃₈ are attributed to the loss of oxygen accompanied by decomposition of these compounds to Sr₂UO₇-x, Sr₂U₃O₁₁-x, and Sr₂U₅O₁₂-x+U₂O₅-x respectively as confirmed from X-ray and chemical analysis (Fig. 1 and Table 1).

The results of the differential thermal analysis of strontium uranates studied up to 1573 K in air showed the absence of DTA peaks for the compounds Sr₃UO₆, Sr₂U₂O₇, SrUO₄ and Sr₂U₅O₁₈. However, in the case of Sr₃UO₆ and Sr₂U₇O₁₂ DTA peaks were observed (Fig. 2).

The compound Sr₃UO₆ showed an endothermic peak with a peak width from 1473 to 1503 K during

![Fig. 1 — Schematic representation of the phase analysis in the system SrO-UO₂ in air](image)

Table 1: Strontium to Uranium Ratios, Oxygen to Uranium Ratios, Designated Compositions and the Cell Parameters of Strontium Uranates Heated for 24 hr in Air in the Temperature Range of 1273-1673 K

<table>
<thead>
<tr>
<th>Heated at (K)</th>
<th>Sr/U (obs)</th>
<th>O/U (obs)</th>
<th>Designated composition</th>
<th>Crystal symmetry</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273</td>
<td>3.00±0.01</td>
<td>3.00±0.01</td>
<td>Sr₂UO₄</td>
<td>Monoclinic</td>
<td>0.5964</td>
<td>0.6201</td>
<td>0.8548</td>
<td>90.32</td>
<td>-</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1673</td>
<td>3.00±0.01</td>
<td>3.00±0.01</td>
<td>Sr₂UO₄</td>
<td>do</td>
<td>0.5964</td>
<td>0.6179</td>
<td>0.8558</td>
<td>90.19</td>
<td>-</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1273</td>
<td>2.00±0.01</td>
<td>3.00±0.01</td>
<td>Sr₂U₂O₅</td>
<td>Monoclinic</td>
<td>0.8111</td>
<td>0.5653</td>
<td>1.1929</td>
<td>108.63</td>
<td>-</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>1673</td>
<td>2.00±0.01</td>
<td>3.00±0.01</td>
<td>Sr₂U₂O₅</td>
<td>do</td>
<td>0.8109</td>
<td>0.5657</td>
<td>1.1920</td>
<td>108.95</td>
<td>-</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>1473</td>
<td>1.50±0.01</td>
<td>3.00±0.01</td>
<td>Sr₂U₄O₁₁</td>
<td>Orthorhombic</td>
<td>1.0525</td>
<td>0.7951</td>
<td>0.8003</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1603</td>
<td>1.50±0.01</td>
<td>3.00±0.01</td>
<td>Sr₂U₄O₁₁</td>
<td>do</td>
<td>1.0633</td>
<td>0.7943</td>
<td>0.7990</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1273</td>
<td>1.00±0.01</td>
<td>3.00±0.01</td>
<td>SrUO₄</td>
<td>Orthorhombic</td>
<td>0.5478</td>
<td>0.7961</td>
<td>0.8117</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1673</td>
<td>1.00±0.01</td>
<td>2.61±0.05</td>
<td>Sr₃O₅UO₄</td>
<td>Rhombohedral</td>
<td>0.6540</td>
<td>0.6540</td>
<td>0.6540</td>
<td>35.85</td>
<td>35.85</td>
<td>35.85</td>
<td>1</td>
</tr>
<tr>
<td>1273</td>
<td>0.67±0.01</td>
<td>2.99±0.02</td>
<td>Sr₂O₅UO₄</td>
<td>Triclinic pseudoorthorhombic</td>
<td>0.6489</td>
<td>0.6530</td>
<td>0.6487</td>
<td>35.41</td>
<td>36.08</td>
<td>35.44</td>
<td>1</td>
</tr>
<tr>
<td>1673</td>
<td>0.67±0.01</td>
<td>2.84±0.03</td>
<td>Sr₂O₅UO₄</td>
<td>do</td>
<td>0.6484</td>
<td>0.6503</td>
<td>0.6482</td>
<td>35.64</td>
<td>35.89</td>
<td>35.65</td>
<td>1</td>
</tr>
<tr>
<td>1273</td>
<td>0.25±0.01</td>
<td>2.95±0.02</td>
<td>Sr₃O₅UO₄</td>
<td>Monoclinic pseudoorthorhombic</td>
<td>0.6730</td>
<td>0.4192</td>
<td>0.4070</td>
<td>90.09</td>
<td>-</td>
<td>2</td>
<td></td>
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</table>
heating with $\Delta H$ of 519.1 Joules/mole and an exo­thermic peak with a peak width from 1368 to 1333 K during cooling with $\Delta H$ of 374.4 Joules/mole. The transition temperatures during heating and cooling were respectively 1493 K and 1358 K. The difference in $\Delta H$ observed during heating and cooling runs could be due to the reverse reaction being sluggish during cooling resulting in loss in the observed $\Delta H$. Also the base line does not remain flat and hence tapers off. Hence, the peak area could be in error. These peaks are attributed to the reversible crystallographic transition of $\text{Sr}_3\text{U}_6$ (orthorhombic) as found from the high temperature X-ray diffraction studies.

The compound $\text{SrU}_4\text{O}_{12.80}$ showed only an endo­thermic peak with a peak width from 1423 to 1463 K during heating with $\Delta H$ of 548.4 Joules/mole, the decomposition temperature being 1443 K. No exotherm was obtained on cooling. The endothermic peak is attributed to the disproportionation of $\text{Sr}_6\text{U}_{18.160}$ into two phases $\text{Sr}_3\text{U}_3\text{O}_{11}$ and $\text{U}_3\text{O}_{6-8}$ (Fig. 1).

The results obtained with the high temperature X-ray diffractometric studies for the variation of the cell parameters and unit cell volume per molecule of the strontium uranates $\text{Sr}_3\text{U}_6$, $\text{Sr}_4\text{U}_8$, $\text{Sr}_3\text{U}_3\text{O}_{11}$, $\text{SrU}_4$, $\text{Sr}_4\text{U}_8\text{O}_{11}$ and $\text{SrU}_4\text{O}_{12.80}$ as a function of temperature in the range 298-1273 K in air are shown in Figs. 4(i) to (vi) respectively. The cell parameters of all the strontium uranates except $\text{SrU}_4\text{O}_{12.80}$ showed a nearly linear increase with temperature in this range and could be expressed by the following least square fitted equations:

1. $\text{Sr}_3\text{U}_6$:
   \[
   \% \text{expansion} = 11.40 \times 10^{-4}(T-298) + 6.12 \times 10^{-7} (T-298)^2 - 5.37 \times 10^{-10}(T-298)^3 \ldots (1)
   \]

2. $\text{Sr}_4\text{U}_8$:
   \[
   \% \text{expansion} = 9.64 \times 10^{-4}(T-298) + 5.96 \times 10^{-7} (T-298)^2 - 4.21 \times 10^{-11}(T-298)^3 \ldots (2)
   \]

3. $\text{Sr}_3\text{U}_3\text{O}_{11}$:
   \[
   \% \text{expansion} = 7.53 \times 10^{-4}(T-298) + 6.82 \times 10^{-7} (T-298)^2 - 3.76 \times 10^{-10}(T-298)^3 \ldots (3)
   \]

4. $\text{SrU}_4$:
   \[
   \% \text{expansion} = 7.45 \times 10^{-4}(T-298) + 5.96 \times 10^{-7} (T-298)^2 - 3.18 \times 10^{-10}(T-298)^3 \ldots (4)
   \]

5. $\text{Sr}_4\text{U}_8\text{O}_{11}$:
   \[
   \% \text{expansion} = 9.92 \times 10^{-4}(T-298) + 2.97 \times 10^{-7} (T-298)^2 + 5.52 \times 10^{-10}(T-298)^3 \ldots (5)
   \]

6. $\text{SrU}_4\text{O}_{12.80}$:
   \[
   \% \text{expansion} = 1.04 \times 10^{-4}(T-298) + 6.46 \times 10^{-7} (T-298)^2 - 4.07 \times 10^{-10}(T-298)^3 \ldots (6)
   \]

where $T$ is the temperature in K.

The per cent linear thermal expansion of all the strontium uranates increased almost linearly with increase in temperature in range 298-1223 K (Fig. 3). The variation of per cent linear thermal expansion with temperature in this range could be expressed by the following least square fitted equations:

1. $\text{Sr}_3\text{U}_6$:
   \[
   \% \text{expansion} = 11.40 \times 10^{-4}(T-298) + 6.12 \times 10^{-7} (T-298)^2 - 5.37 \times 10^{-10}(T-298)^3 \ldots (1)
   \]

2. $\text{Sr}_4\text{U}_8$:
   \[
   \% \text{expansion} = 9.64 \times 10^{-4}(T-298) + 5.96 \times 10^{-7} (T-298)^2 - 4.21 \times 10^{-11}(T-298)^3 \ldots (2)
   \]

3. $\text{Sr}_3\text{U}_3\text{O}_{11}$:
   \[
   \% \text{expansion} = 7.53 \times 10^{-4}(T-298) + 6.82 \times 10^{-7} (T-298)^2 - 3.76 \times 10^{-10}(T-298)^3 \ldots (3)
   \]

4. $\text{SrU}_4$:
   \[
   \% \text{expansion} = 7.45 \times 10^{-4}(T-298) + 5.96 \times 10^{-7} (T-298)^2 - 3.18 \times 10^{-10}(T-298)^3 \ldots (4)
   \]

5. $\text{Sr}_4\text{U}_8\text{O}_{11}$:
   \[
   \% \text{expansion} = 9.92 \times 10^{-4}(T-298) + 2.97 \times 10^{-7} (T-298)^2 + 5.52 \times 10^{-10}(T-298)^3 \ldots (5)
   \]

6. $\text{SrU}_4\text{O}_{12.80}$:
   \[
   \% \text{expansion} = 1.04 \times 10^{-4}(T-298) + 6.46 \times 10^{-7} (T-298)^2 - 4.07 \times 10^{-10}(T-298)^3 \ldots (6)
   \]

where $T$ is the temperature in K.
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![Graph showing temperature changes for different strontium uranates.](image-url)
Fig. 5: Variation of Unit Cell Volume of Strontium Uranates as a Function of Temperature for (I) Sr$_3$UO$_6$, (II) Sr$_2$UO$_5$, (III) Sr$_3$U$_2$O$_{11}$, and (IV) Sr$_4$U$_4$O$_{12}$.80.
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![Graph](image)

**Table 2** — COEFFICIENTS OF AVERAGE LINEAR THERMAL EXPANSION (\(\alpha_l\)) OBTAINED FROM DILATOMETRIC STUDIES AND THE COEFFICIENTS OF AVERAGE VOLUME THERMAL EXPANSION (\(\alpha_v\)) OBTAINED FROM HIGH TEMPERATURE X-RAY DIFRACTOMETRIC STUDIES FOR THE STRONTIUM URANATES

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Compound</th>
<th>Crystal symmetry</th>
<th>(\alpha_l) (\times 10^{-6}) K(^{-1})</th>
<th>(\alpha_v) (\times 10^{-6}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sr(_3)UO(_6)</td>
<td>Monoclinic</td>
<td>12.5</td>
<td>29.4</td>
</tr>
<tr>
<td>2</td>
<td>Sr(_2)UO(_5)</td>
<td>Orthorhombic</td>
<td>11.1</td>
<td>33.9</td>
</tr>
<tr>
<td>3</td>
<td>Sr(_2)UO(_5)</td>
<td>Orthorhombic</td>
<td>10.6</td>
<td>31.7</td>
</tr>
<tr>
<td>4</td>
<td>Sr(_2)UO(_5)</td>
<td>Orthorhombic</td>
<td>10.3</td>
<td>33.0</td>
</tr>
<tr>
<td>5</td>
<td>Sr(_3)UO(_5.80)</td>
<td>Triclinic pseudo-orthorhombic</td>
<td>17.4</td>
<td>47.2</td>
</tr>
<tr>
<td>6</td>
<td>Sr(_3)UO(_5.80)</td>
<td>Monoclinic pseudo-orthorhombic</td>
<td>3.5</td>
<td>13.7</td>
</tr>
</tbody>
</table>

The unit cell volume per molecule of all the strontium uranates except Sr\(_3\)UO\(_5.80\) increased normally and almost linearly with increase in temperature (Fig. 5(i) to (v)). For the compound Sr\(_3\)UO\(_5.80\), however, the unit cell volume increased very gradually. The gradual increase in unit cell volume of Sr\(_3\)UO\(_5.80\) as compared to other strontium uranates is attributed to the peculiar variation of \(a\), \(b\) and \(c\) axis as shown in Fig. 4(vi).

The values of the coefficients of average linear and volume thermal expansion are given in Table 2 and plotted in Fig. 6 as a function of composition (mole % U\(_2\)O\(_5\)).

As can be seen from Table 2 and Fig. 6 the coefficients of average linear as well as volume thermal expansion for the strontium uranates Sr\(_3\)UO\(_6\), Sr\(_2\)UO\(_5\), Sr\(_2\)UO\(_5.80\) and SrUO\(_4\) are very nearly the same [\(\alpha_l = 10-13 \times 10^{-6}\) K\(^{-1}\) and \(\alpha_v = 29-33 \times 10^{-6}\) K\(^{-1}\)]. However, for the compound Sr\(_3\)UO\(_5.80\) both these coefficients show an increase (\(\alpha_l = 17-4 \times 10^{-6}\) K\(^{-1}\) and \(\alpha_v = 47-2 \times 10^{-6}\) K\(^{-1}\)) and for the compound Sr\(_3\)UO\(_5.80\) the coefficients of expansion show a sudden decrease (\(\alpha_l = 3-5 \times 10^{-6}\) K\(^{-1}\) and \(\alpha_v = 13-7 \times 10^{-6}\) K\(^{-1}\)). Thus amongst all the strontium uranates, the thermal expansion coefficient of Sr\(_3\)UO\(_5.80\) is maximum and that of SrUO\(_4\) is minimum (Fig. 6).

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**References**


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